Entanglements and cross-links in ultra-high molecular weight polyethylene

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SUMMARY

This thesis deals with the results of an investigation on the influence of chain entanglements and cross-links in ultra-high molecular weight polyethylene (UHMWPE), on the crystallization behaviour of the bulk polymer, and on the material properties of highly oriented gel-spun hot-drawn UHMWPE fibres.

The average chain length between entanglements in linear polyethylene is about 18 nm, a distance comparable to the fold-length of the lamellae in crystallized polyethylene. The entanglements move to the fold surface upon crystallization, because they cannot be incorporated inside the crystal-lattice due to their dimensions. Because of this, the high concentration of entanglements has almost no influence on the melting temperature of the lamellae.

The mobility of the entanglements can be reduced by cross-linking of the polyethylene molecules in the melt, by means of high energy electron beam irradiation (**chapter 2**). The reduction of the mobility by means of cross-links resulted in a decrease of the lamellae dimensions with increasing irradiation dose, both in the chain direction and in the directions perpendicular to it. This resulted in a melting point depression, which is described in chapter 2 with both the Gibbs-Thomson relationship and the lattice theory of Flory. It was possible to calculate the entanglement concentration by means of equilibrium swelling experiments. From these experiments, an average molecular weight between the entanglements of 4700 kg/kmol was found. These swelling measurements also gave information about the number of cross-links produced per 100 eV absorbed irradiation energy. The G(cross-link) value of 2.6 / 100 eV shows that the G-value is not a material constant, but that it depends on the morphology of the polymeric material.

The number of chain scissions caused by the irradiation of the melt was found to be zero, probably because of a cage recombination reaction, due to the high viscisity of the polymer melt.

Gel-spun hot-drawn UHMWPE fibres, consist of almost completely extended chain between the entanglements. As mentioned above, the entanglements cannot be incorporated inside the crystal lattice. This results in a structure of large crystalline blocks, between which small disordered domains are sandwiched. These disordered domains contain the entanglements and other crystal defects. The dimensions of the crystalline blocks and the disordered domains determine the Young's modulus of the fibre (**chapter 4**). Due to the fact that the disordered domains are the weak links in the fibre, these domains will elongate more than the crystalline blocks upon tensile deformation, which results in a relativel

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which results in a relatively small elongation at break of the polyetylene fibre.

The irradiation of ultra-high strength UHMWPE fibres resulted in an exponential reduction of the tensile strength with increasing irradiation dose (**chapter 3**). From this exponential reduction, the number of load carrying chains per disordered domain could be calculated, which yielded for a fibre with an initial tensile strength of 3 GPa a number of 150 load carrying chains. This means that if all the chains in the disordered domain had been load carrying, than the tensile strength would have been about 22 GPa, a value comparable to the theoretical strength of the carbon-carbon bond strength.

The shrinkage of gel-spun hot-drawn UHMWPE fibres was found to be strongly influenced by the entanglements (**chapter 5**). Fibres hot-drawn beyond the natural draw ratio displayed a ribbon shaped melting front upon melting. The ribbon shaped melting has been explained by the high orientation of the fibre. Entropically it is probably more favourable for the fibre to melt in a direction perpendicular to the fibre axis.

Shrinkage experiments where the fibres were constrained preheated before shrinkage was allowed, displayed cylindrical shrinkage. From the shrinkage ratio measured in this way, it was concluded that the entanglement concentration in the disordered domains is very high, and that the shrinkage is almost completely due to the shrinkage of the crystalline blocks.

Annealing experiments of gel-spun hot-drawn UHMWPE fibres, at temperatures near the orthorhombic-hexagonal phase transition temperature (**chapter 6**), yielded a reduction of the Young's modulus, and an increase in elongation at break from 3 % to 6 %. The tensile strength, however, did not change upon annealing, meaning that the length distribution of taut tie molecules between the crystalline block didn't become more homogeneous. This in contradiction to what one would expect, and measured for other polymers such as Nylon-6.

The tensile strength of gel-spun hot-drawn UHMWPE fibres as a function of the tensile testing temperature could be devided in two temperature regions (**chapter 7**). At temperatures beyond 20 °C, the tensile strength has been found to depend on a stress induced orthorhombic-hexagonal phase transition, leading to a rotator phase where the chains can easily slip past one another. Below 20 °C, chain scissioning has been found to determine the tensile strength of the polyethylene fibres. The tensile testing data were treated with the kinetic fracture model of Zhurkov. The activation energy for bond fracture and the corresponding activation volume were determined for this temperature region. From these values, together with the data from the previous chapters, it was concluded that the tensile strength of the ultra-high strength polyethylene fibres is determined by the relatively weak entanglements in the disordered domains.

Porous gel-spun UHMWPE fibres yielded a measurable gel-fraction only at relatively high irradiation doses **(chapter 8)**. Equilibrium swelling measurements showed that the G(x) value for the production of cross-links, was about the value expected, namely G(x) = 1.3 / 100 eV. The G(x) value calculated from the gel-point irradiation dose was only 0.06 / 100 eV. Comparing of the data from equilibrium swelling experiments and sol-gel measurements led to the conclusion that taut tie molecules are preferentially scissioned upon irradiation, thereby separating the lamellae. At higher irradiation doses, the lamellae will be connected again by means of cross-links between consecutive lamellae, leading to a measurable gel-fraction.

Verhakingen en vernettingspun

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van ketenverhakingen en chemi
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